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A CATALOG OF OPTICAL EXTINCTION DATA FOR VARIOUS AEROSOLS/SMOKES

Edgewood Arsenal
Aberdeen Proving Ground, Maryland

**JUNE 1976** 

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# A CATALOG OF OPTICAL EXTINCTION DATA FOR VARIOUS AEROSOLS/SMOKES

by

Marrill Milham

Development and I ngineering Directorate

June 1976





DEPARTMENT OF THE ARMY
Headquarters, Edgewood Arsenal
Aberdeen Proving Ground, Maryland 21010



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#### 20. ABSTRACT (Continue on poverse side if necessary and identify by bloch number)

Extinction spectra in the 3- to 5-, 8- to 13-, and 0.4 to 2.4- $\mu$ m spectral region have been obtained for FS, red phosphorus, HC, and fog oil smokes. A limited number of theoretical predictions based on Mie theory are also presented and compared with the experimental results. The experimental and computational procedures are described in some detail.

These findings are subject to revision; the final report will be published later.

#### **PREFACE**

This report summarizes the status of work performed under Task 1L662619AO6504, Flame. Incendiary, and Smoke Technology. The work was performed during the period of 22 August 1975 through 5 December 1975.

These findings are subject to revision; the final report will be written later.

Publication of this report will make available to the user community extinction spectra of common military aerosol/smokes. These data will be updated from time to time as the experimental program progresses.

Extinction data such as those reported here are fundamental to military screening and countermeasuring involving electro-optical systems operating in the visible and infrared wavelengths.

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# A CATALOG OF OPTICAL EXTINCTION DATA FOR VARIOUS AFROSOLS/SMOKES

#### 1. INTRODUCTION.

Over the past several months a team of scientific investigators at Edgewood Arsenal has performed a substantial number of optical extinction measurements on various aerosols/smokes. The purpose of this document is to communicate, in an informal and flexible manner, the results of these measurements. A limited number of theoretical predictions based on Mie calculations are also presented and are compared with the experimental results.

Figure 1 shows the basic experimental arrangement which has been employed and also the Exotech radiometer which scans the 3- to 5- and 8- to 13- $\mu$ m regions. (In many instances, data outside the 8- to 13- $\mu$ m region are presented, but these are considered  $\epsilon$  be somewhat less reliable than the 8- to 13- $\mu$ m data.) Not shown, but set up in a similar fashion are a Perkin Elmer 12C spectrometer with a tungsten lamp source (0.4- to 2.4- $\mu$ m spectral range) and a .63- $\mu$ m Helium-Neon laser power meter combination.

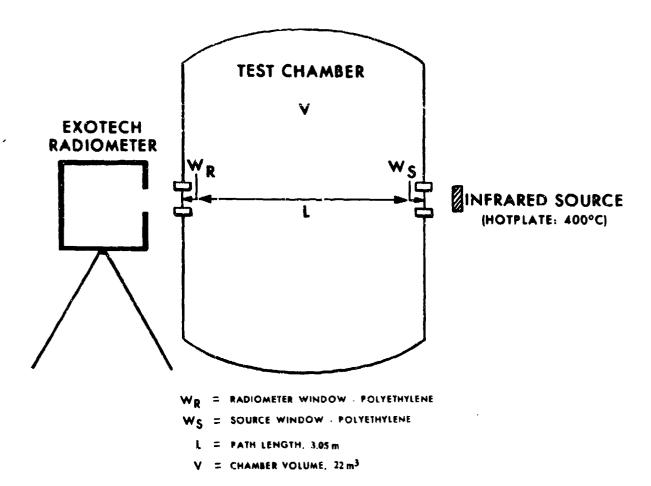


Figure 1. Experimental Arrangement

The usual experimental procedure is as follows:

- 1. Make a spectral scan of the empty chamber to determine the unattenuated source intensity.
- 2. Disseminate the smoke precursor in an appropriate manner (as shown in appendix A).
  - 3. Stir the smoke for sever: ninutes to produce a homogeneous concentration.
- 4. Make spectral scans (Exotech radiometer, Perkin Elmer 12C), determine particle size distribution (Andersen impactor), and determine airborne concentration (glass fiber filter samples).
  - 5. Repeat steps 3, 4, and 5 as many times as practicable.
  - 6. Empty the cnamber of smoke and repeat step 1.

The data obtained from the test are then analyzed according to the data processing procedures which we have developed and implemented over the past several months.

The equations used in reducing the spectral data are described in the summary of useful equations, below.

Summary of Useful Equations (See appendix B for details.)

$$T = I/I_0 \tag{1}$$

T = transmittance

I = measured intensity with aerosol in chamber

 $I_0$  = measured intensity with no aerosol in chamber

$$T = e^{-aCL}$$
 (2)

 $\alpha$  = extinction coefficient,  $m^2/gm$ 

 $C = aerosol concentration, gm/m^3$ 

L = path length, m

$$a = \frac{3}{2} \frac{Q_e}{\rho D} \tag{3}$$

Qe = efficiency factor - ratio of effective "optical area" to geometrical area

 $\rho = \text{density}, \text{gm/cm}^3$ 

 $D = particle diameter in micrometers (<math>\mu m$ )

These equations also provide the interface between the Mie modeling calculations and the experimental measurements. A simple derivation of these relationships is presented in appendix B. The current data processing methodology is succinctly described in the flow chart (figure 2). The left-hand portion of the flow chart describes the processing of the experimental data while the right-hand portion describes the Mie modeling process. The results of the experiment and the model are compared (center of the flow chart) by computing and plotting a difference spectrum; i.e., the computed values of the extinction coefficient, a, are subtracted wavelength by wavelength from the experimental values and plotted. The complete data processing cycle has been carried out for only one smoke material, FS. This limitation has been imposed solely because of the lack of refractive index data for other smokes. The output of the .63-\(mu\) Helium-Neon laser power meter was recorded on a paper chart, and these data were reduced by hand.

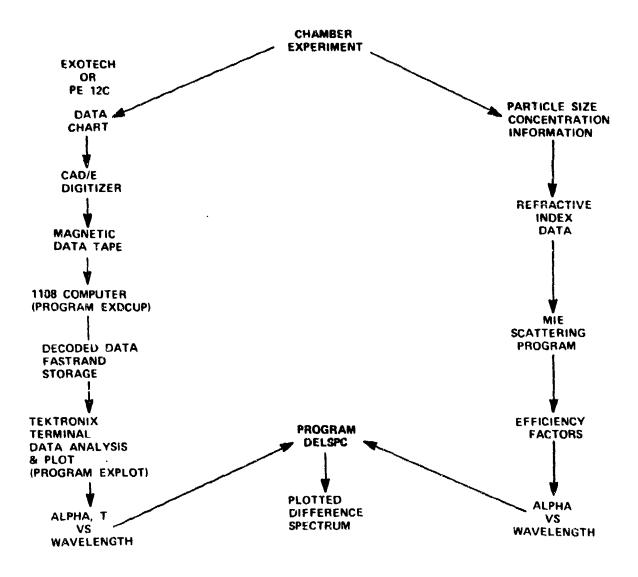


Figure 2. Flow Chart of Data Processing Procedures

The catalog of experimental data is arranged according to the type of smoke precursor and the test date. The data are presented as curves of extinction coefficient, a, plotted as a function of wavelength. The more recent tests (those conducted after the retrofitting of the radiometer CVF) include data for the 3- to 5- $\mu$ m region in addition to the 8- to 13- $\mu$ m data. The 3- to 5- $\mu$ m data have been edited so remove the spectral effects of the polyethylene windows (3.2 to 3.8  $\mu$ m) and atmospheric CO<sub>2</sub> (4.1 to 4.4  $\mu$ m).

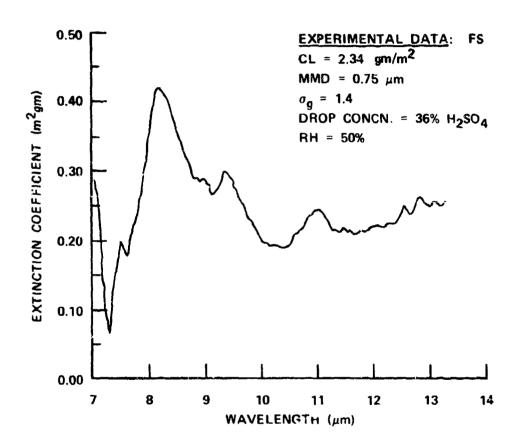
The upper right corner of each experimental curve contains the following:

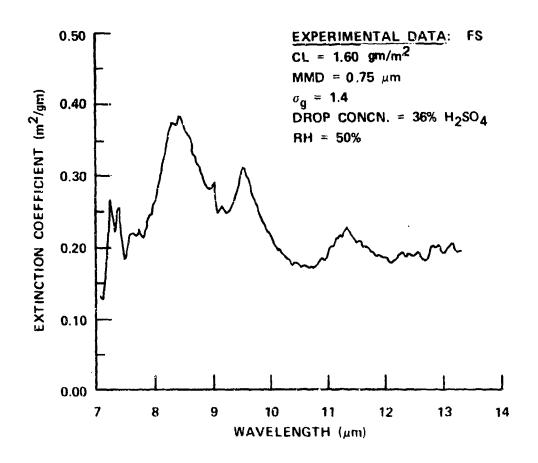
- 1. Smoke designator (see appendix A)
- 2. The value of the product of the airborne concentration and the optical path length (CL)
  - 3. The mass median diameter of the aerosol (MMD)
  - 4. The geometric standard deviation  $(\sigma_g)$  of the aerosol
  - 5. The airborne droplet concentration
  - 6. The percent relative humidity (RH)

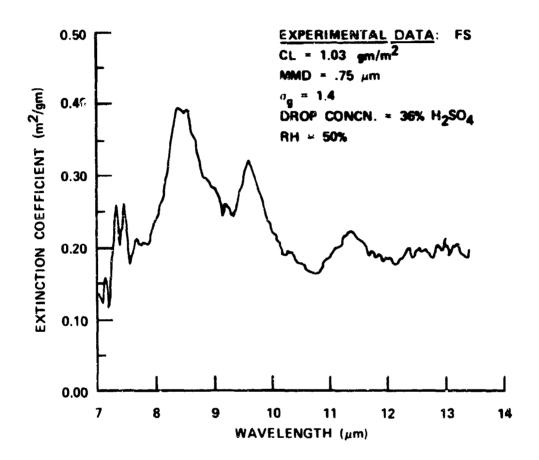
The data catalog will be updated from time to time as the experimental program progresses.

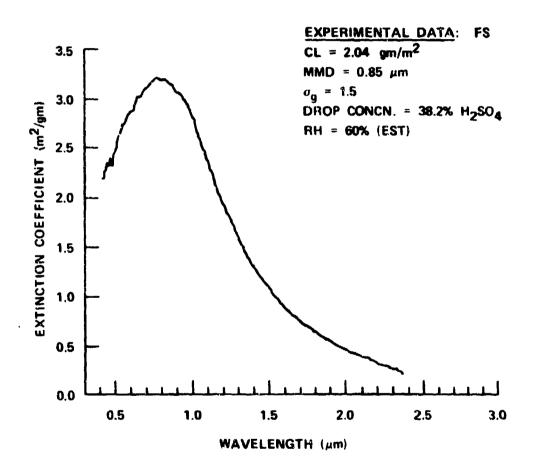
#### II. FS SMOKE (CHLOROSULFONIC ACID + FREE SO<sub>3</sub>) EXPERIMENTAL DATA.

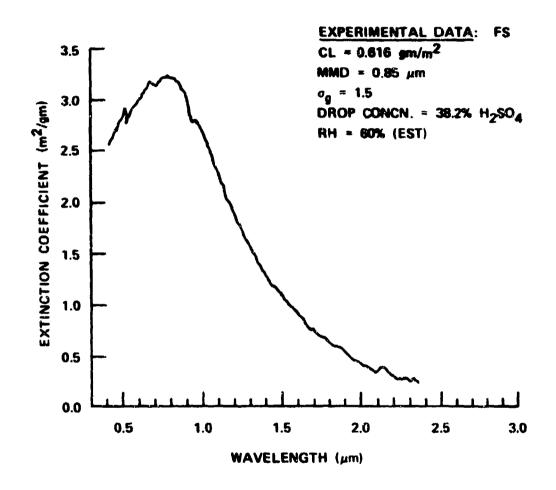
1. FS Smoke, 8 to 13 μm, Test Date: 22 August 1975.

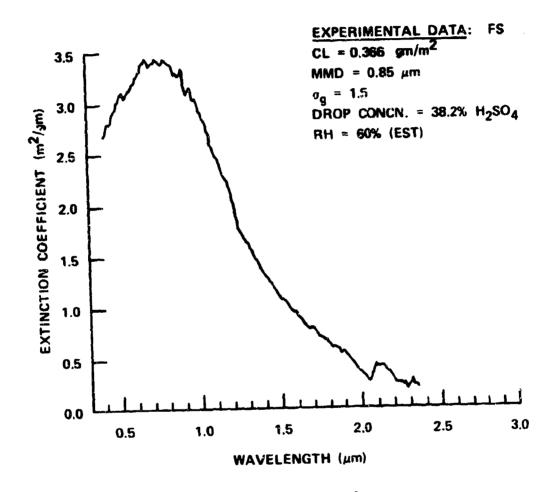


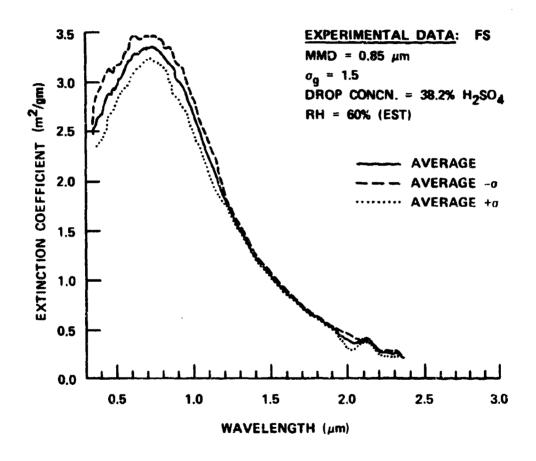


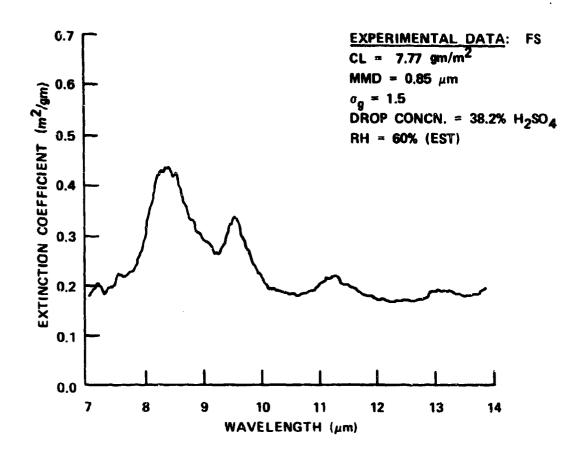




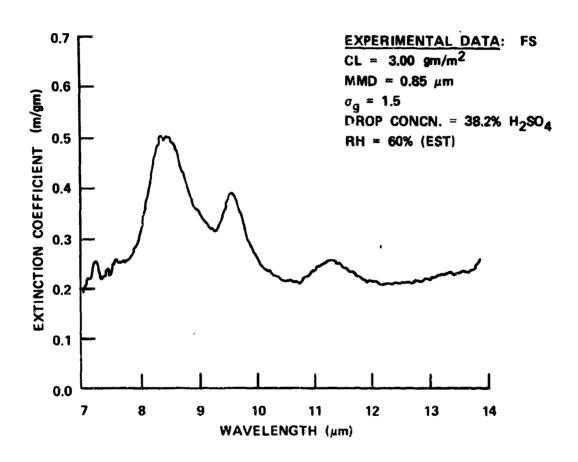


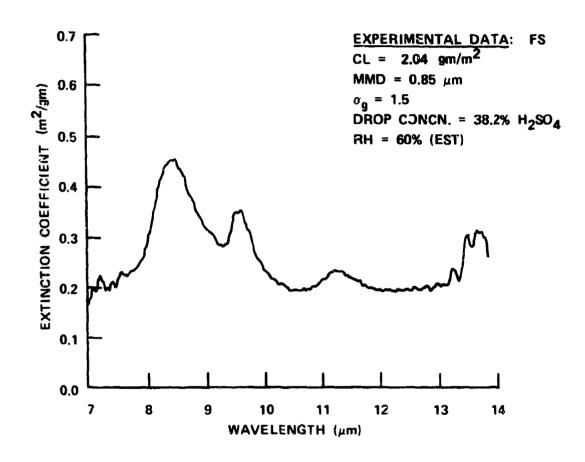


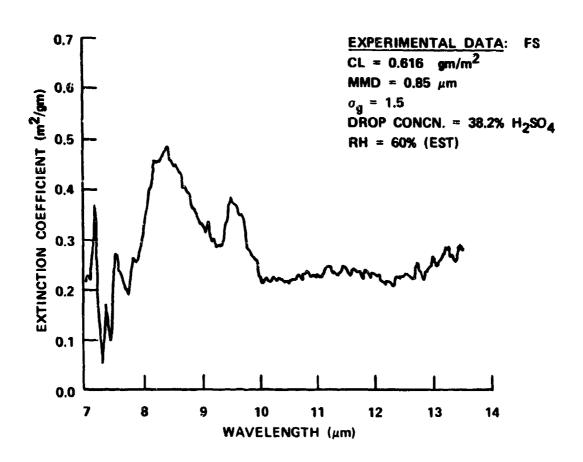


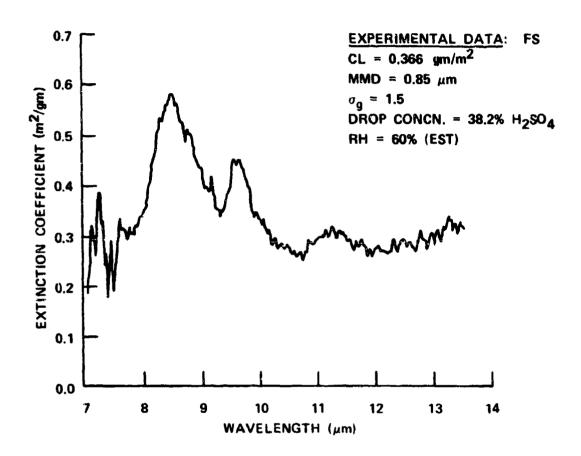


( a )







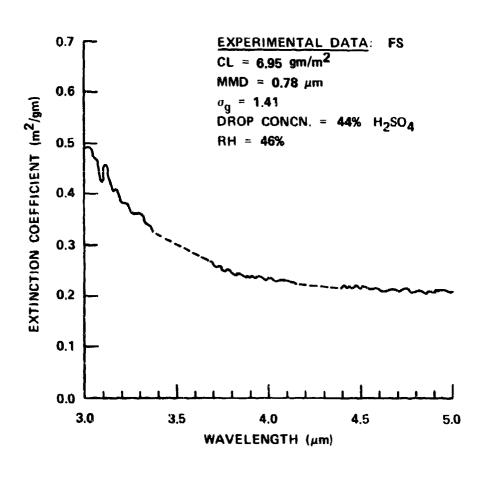


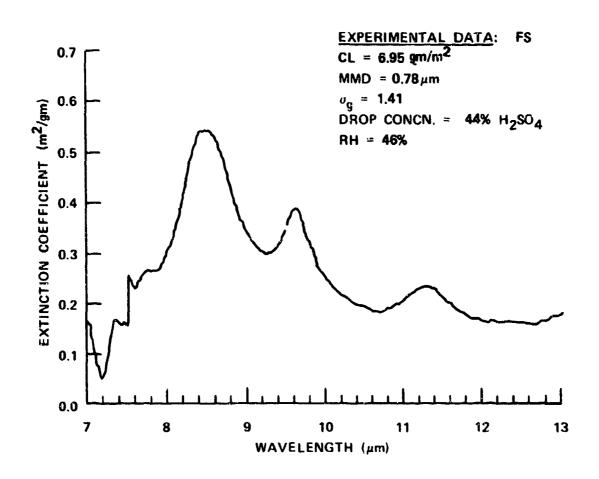
24<sub>5</sub>

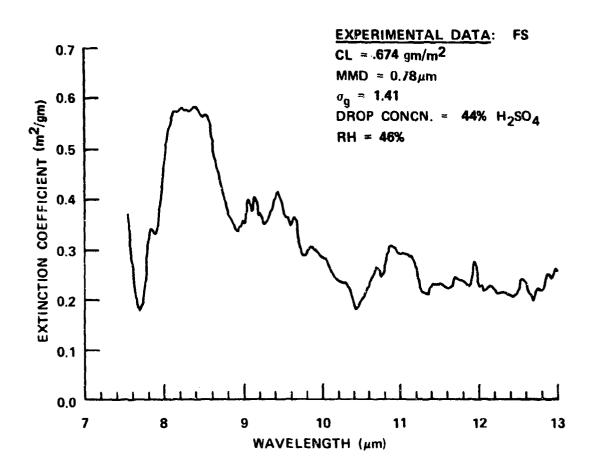
## 3. FS Smoke, 3 to 5 $\mu$ m and 8 to 13 $\mu$ m. Test Date: 19 November 1975.

Experimental Data: Laser Wavelengths

Wavelength	Extinction coefficient	
μm	m <sup>2</sup> /gm	
.63	4.5	
1.06	2.0	







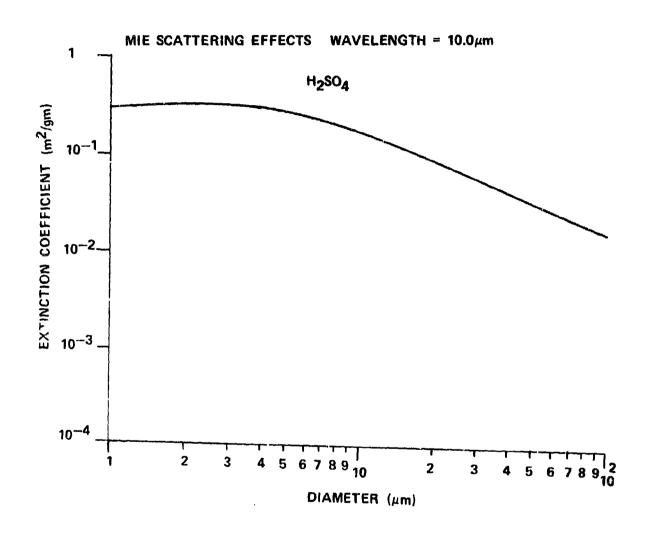
#### III. COMPUTED SPECTRA (Sulfuric Acid: 6 to 14 µm).

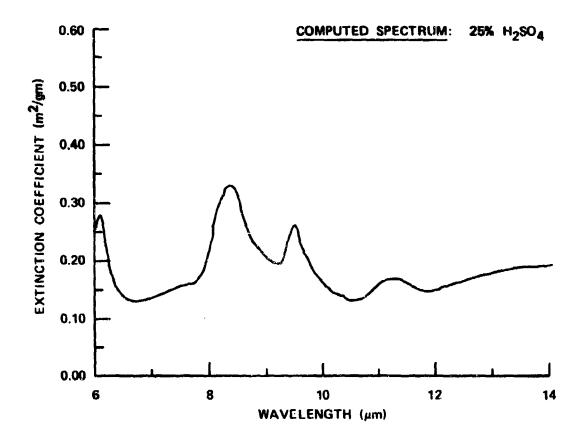
The spectra presented in this section were computed 1 mm the Mie theory. The DBMIE<sup>1</sup> Fortran subroutine, modified for use on the Edgewood Arsenal UNIVAC 1108 computer, was used to make these calculations. The refractive index data input to the subroutine were those of Palmer and Williams.<sup>2</sup> A monodisperse aerosol of 1-µm-diameter particles was assumed.

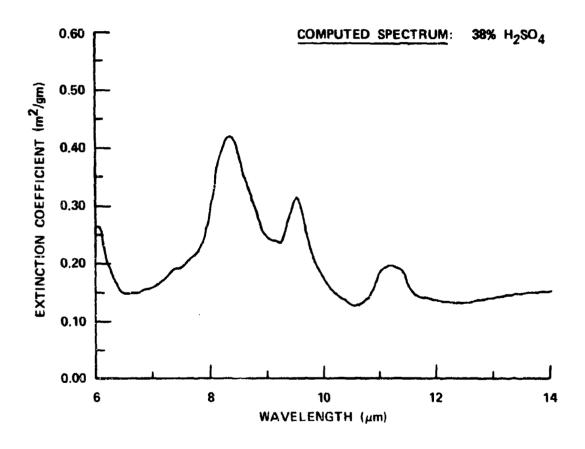
Although it is known that real aerosols are not monodisperse, this does not introduce a significant error in the calculations if the aerosol particles are small enough. This phenomenon is illustrated in the next figure. This is a plot of the extinction coefficient for  $\rm H_2SO_4$  as a function of the particle diameter for an illuminating wavelength of  $10\,\mu\rm m$ . As long as the particle diameter is small, say less than  $5\,\mu\rm m$ , the extinction coefficient is essentially a constant; and the distribution of particle sizes has a minimal effect on the spectrum.

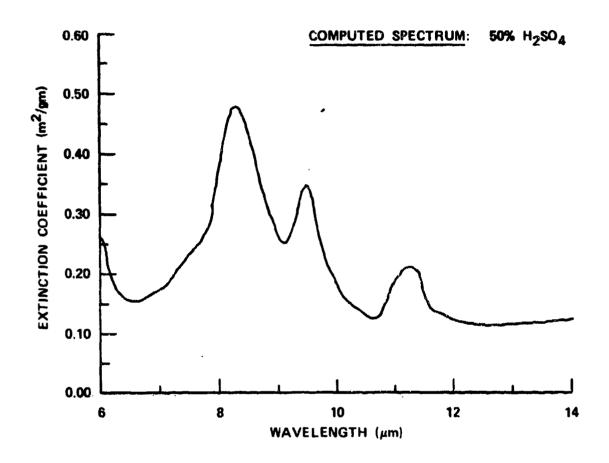
<sup>&</sup>lt;sup>1</sup>Dave, J. V. Subroutines for Computing the Parameters of the Electromagnetic Radiation Scattered by a Sphere IBM Palo Alto Scientific Center Report 320-3237. May 1968.

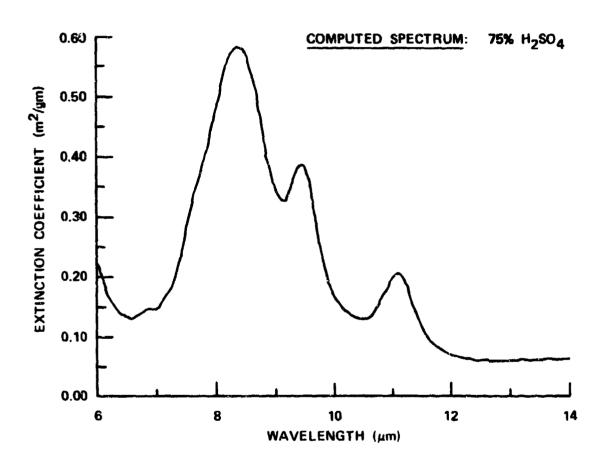
<sup>&</sup>lt;sup>2</sup>Palmer, K. F., and Williams, D. Optical Constants of Sulfuric Acid; Application to the Clouds of Venus? Opt. Soc. Am. 14, 208 (1975).

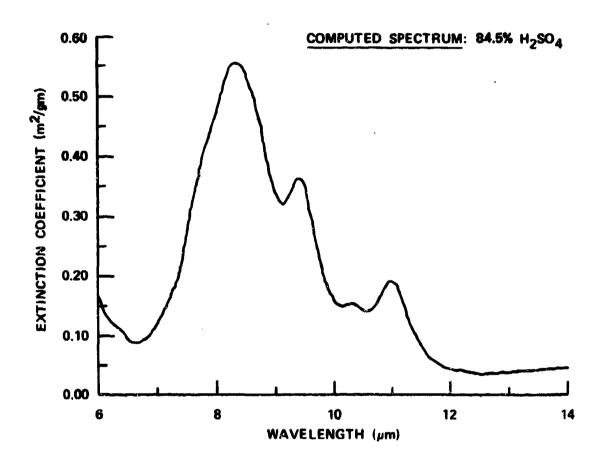


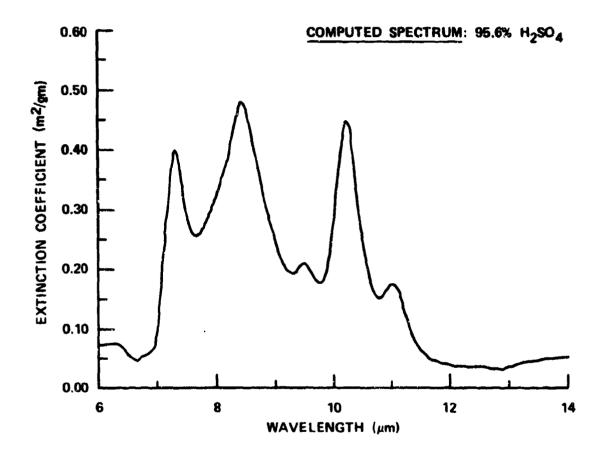












#### IV. DIFFERENCE SPECTRA.

The spectra presented in this section were derived by subtracting the computed value of the extinction coefficient (see Section III) wavelength by wavelength from the experimental values.

These particular data are from the test of 4 September 1975 (Section II) and are further identified by their CL values.

The smoke agent FS is a mixture of chlorosulfonic acid and free sulfur trioxide which reacts with atmospheric moisture as follows:

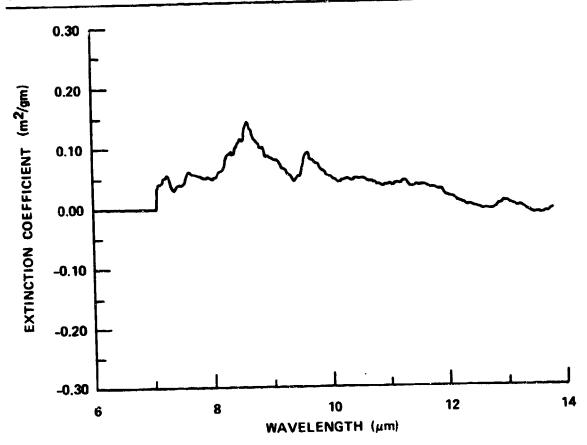
$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$CISO_3H + H_2O \rightarrow HCI + H_2SO_4$$

It has been documented in the literature<sup>3</sup> that sulfuric acid will not nucleate hydrochloric acid. Unless foreign nuclei are introduced, the hydrochloric acid will not aerosolize. Chemical analysis of the aerosols formed in our chamber after disseminating FS confirmed this result. No HCl was found to be present in the aerosol, and no spectral effects which could be ascribed to HCl were found.

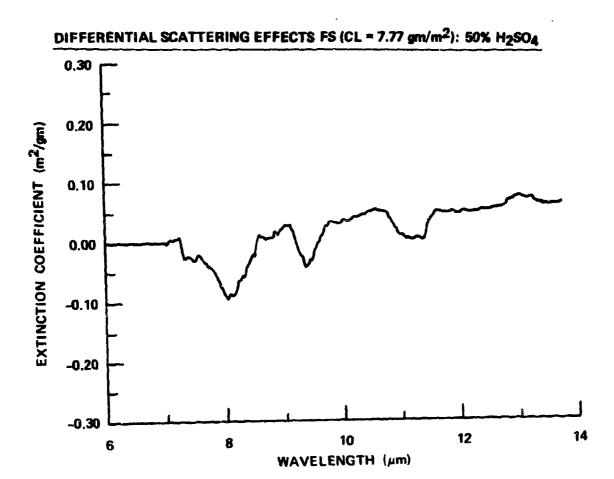
<sup>&</sup>lt;sup>3</sup>Gillespie, G. R., and Johnston, E.H.F. Particle Size Distribution in Some Hygroscopic Aerosols. Chem. Engr. Prog. 51, 74-F (1955).

# DIFFERENTIAL SCATTERING EFFECTS FS (CL = 7.77 gm/m<sup>2</sup>): 25% H<sub>2</sub>SO<sub>4</sub>

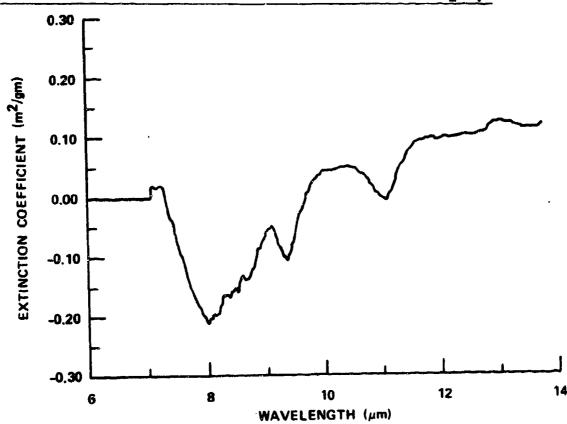


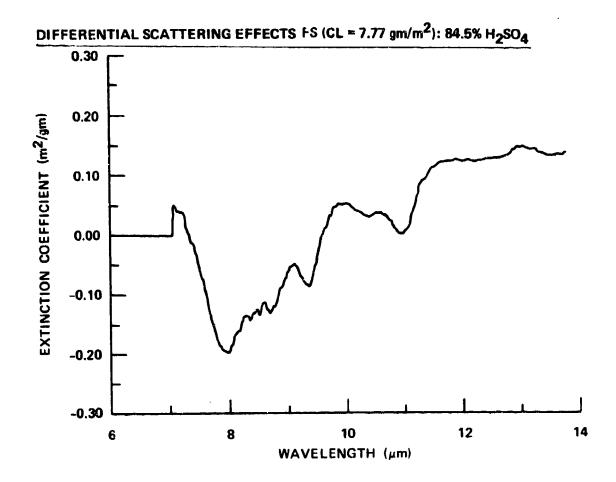
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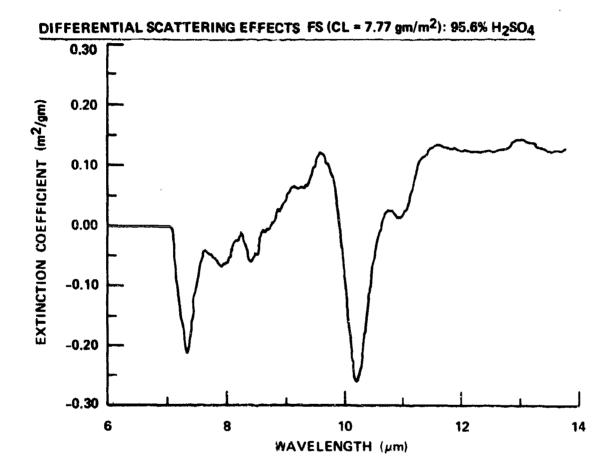
WAVELENGTH (µm)

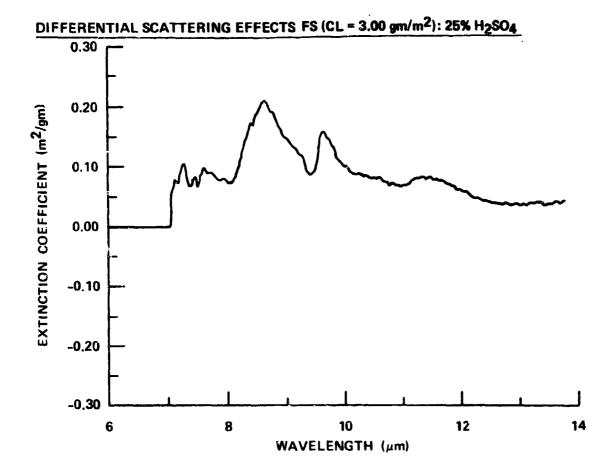


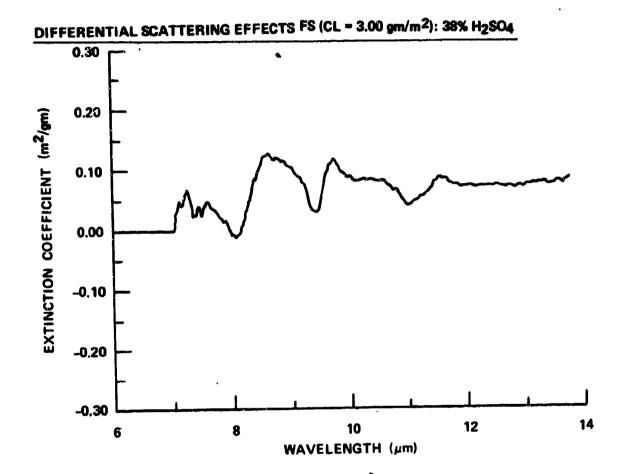
## DIFFERENTIAL SCATTERING EFFECTS FS (CL = 7.77 gm/m²): 75% H2SO4

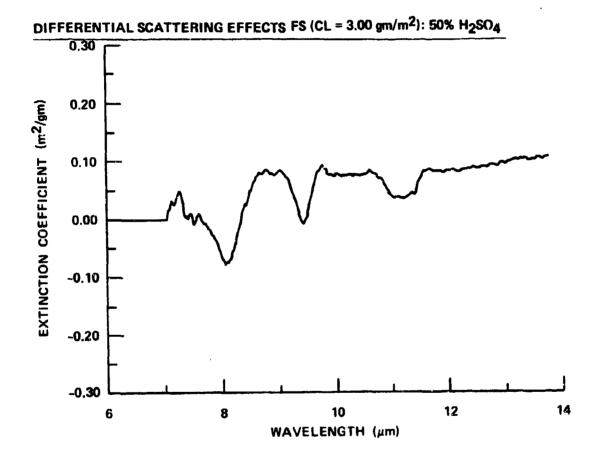












DIFFERENTIAL SCATTER'NG EFFECTS FS (CL = 3.00 gm/m<sup>2</sup>): 75% H<sub>2</sub>SO<sub>4</sub>

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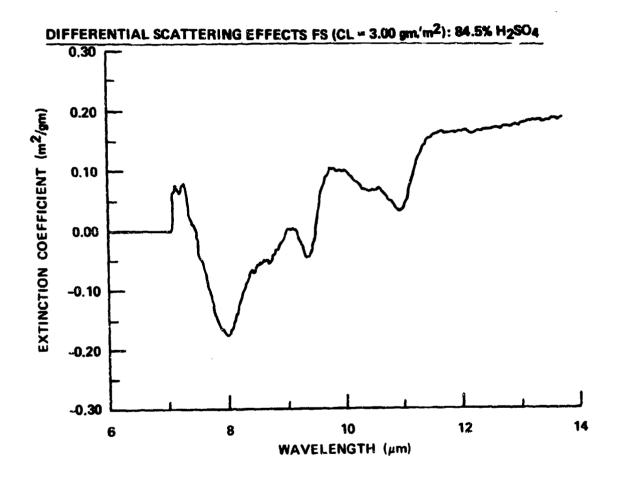
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DIFFERENTIAL SCATTERING EFFECTS FS (CL = 3.00 gm/m²): 96.6% H<sub>2</sub>SO<sub>4</sub>

0.30

0.20

0.10

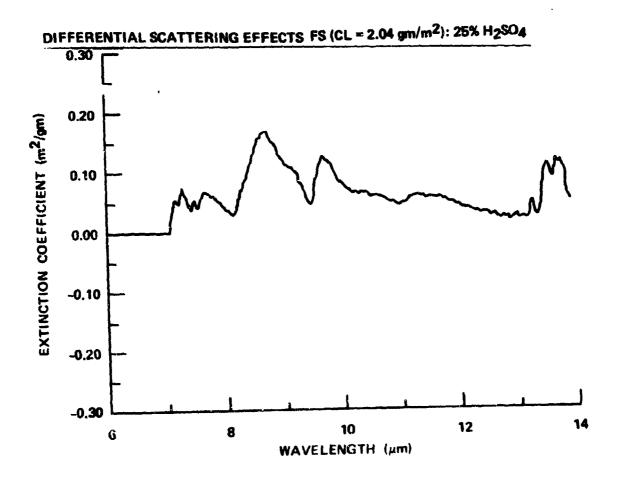
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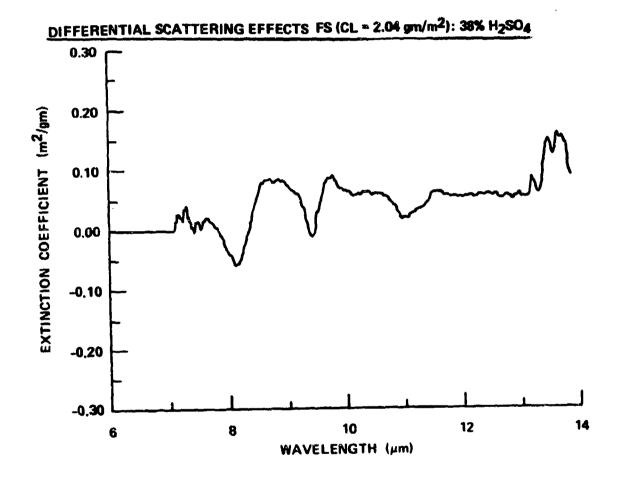
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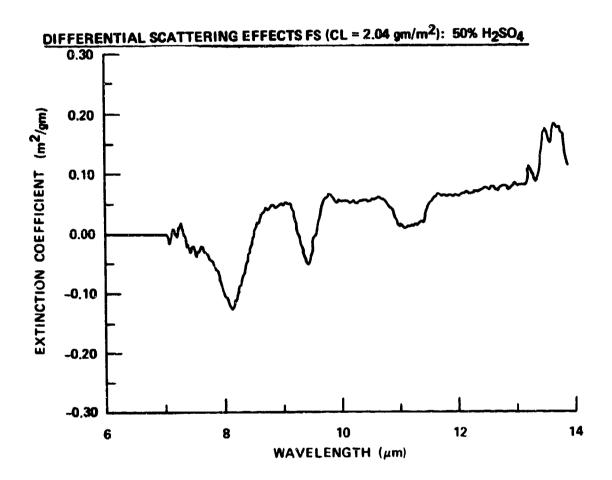
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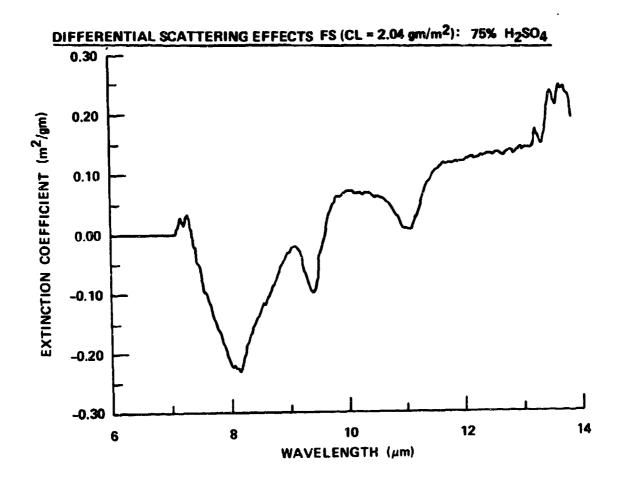
6 8 10 12 14

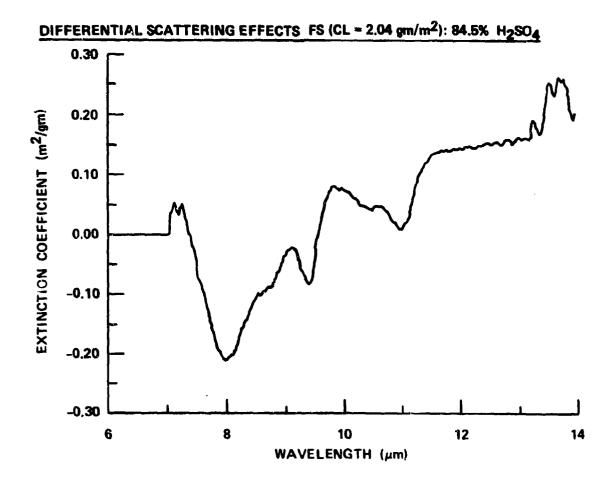
WAVELENGTH (μm)

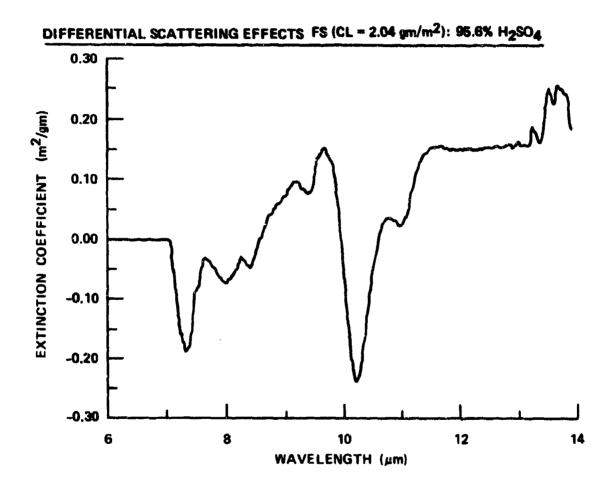






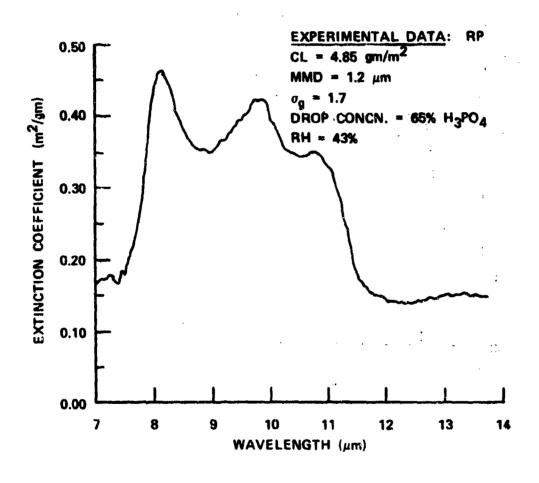


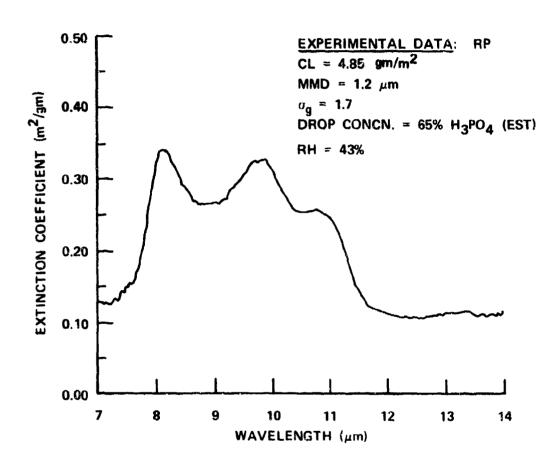


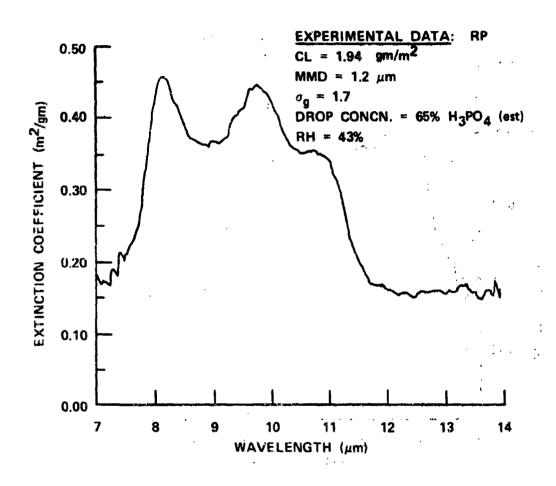


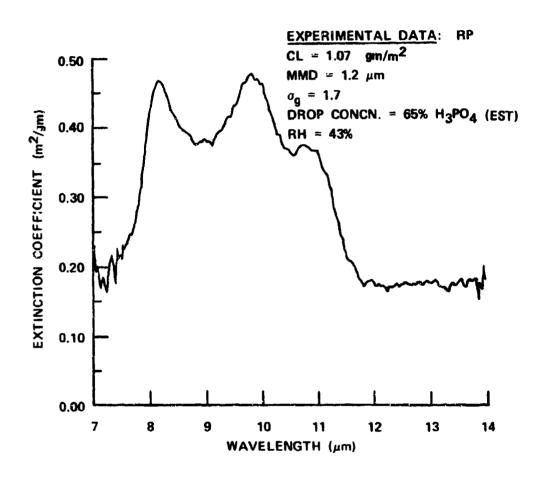
## V. RED PHOSPHORUS (RP) SMOKE EXPERIMENTAL DATA.

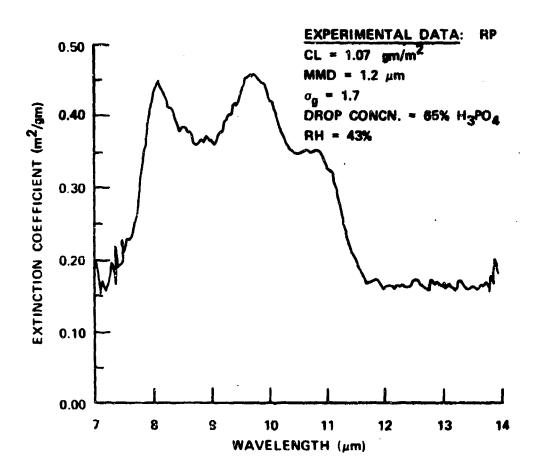
1. RP Smoke, 8 to 13 μm, Test Date: 14 August 1975.

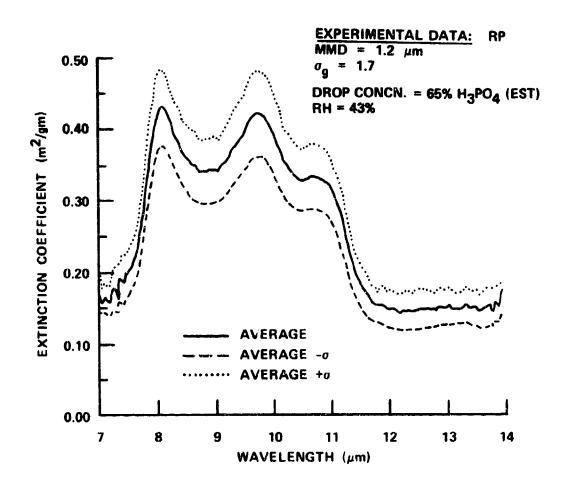






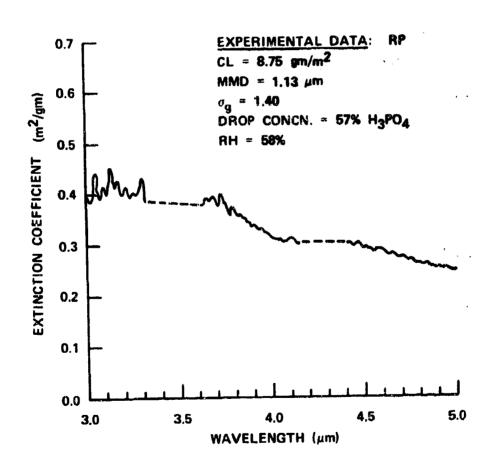


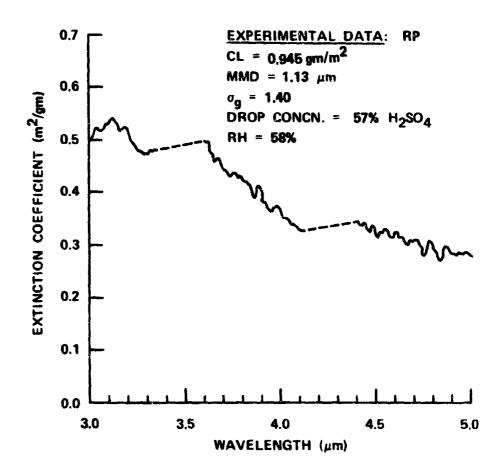


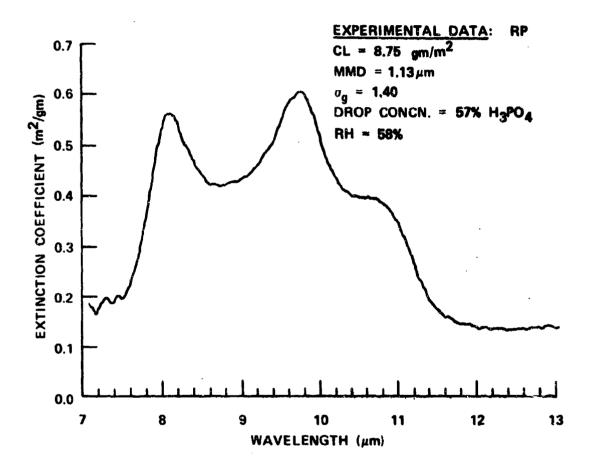


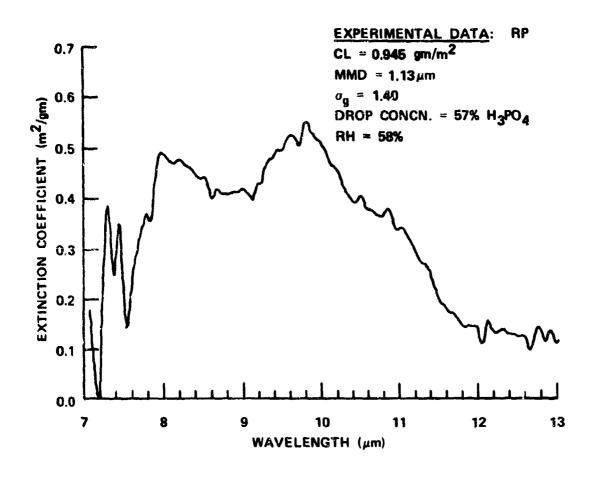
 Red Phosphorus Smoke, 3 to 5 μm and 8 to 13 μm, Test Date: 20 November 1975. Experimental Data: Laser Wavelengths

Wavelength	Extinction coefficient	
μm	m <sup>2</sup> /gm	
.63	1.8	
1.06	1.5	







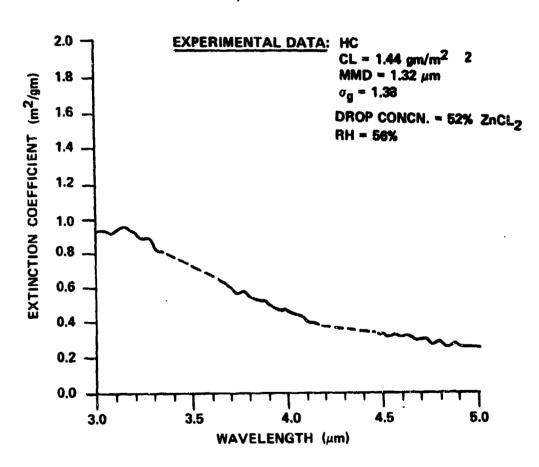


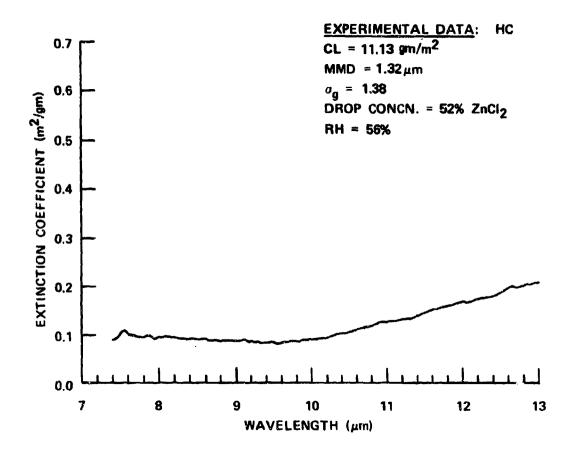
# VI. HC SMOKE (ZINC OXIDE, ALUMINUM, HEXACHLOROETHANE) EXPERIMENTAL DATA, 3 to 5 μm AND 8 to 13 μm, Test Date: 19 November 1975.

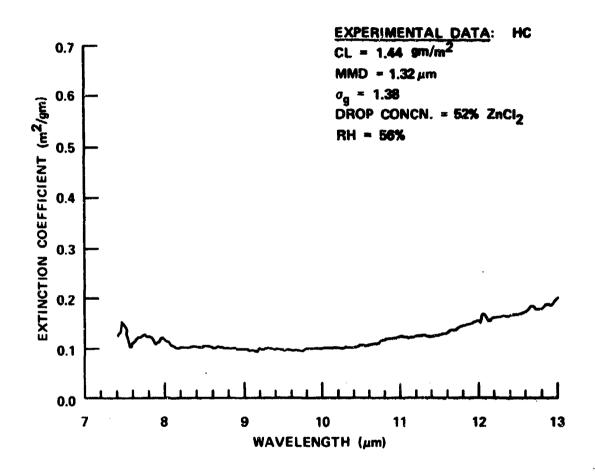
Experimental Data: Laser Wavelengths

Wavelength	Extinction coefficient
μm	m <sup>2</sup> /gm
.63	1.4
1.06	1.5

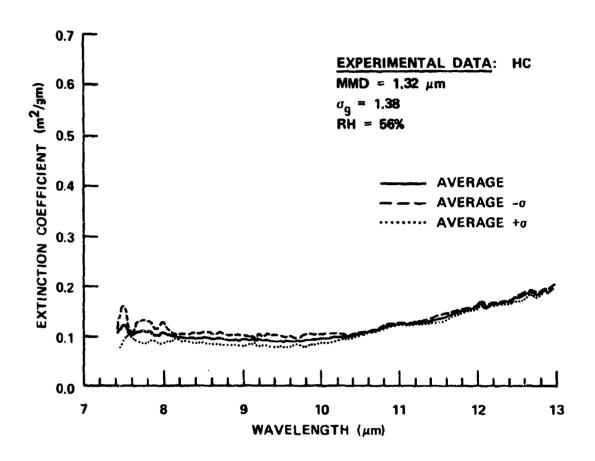
のでは、100mm





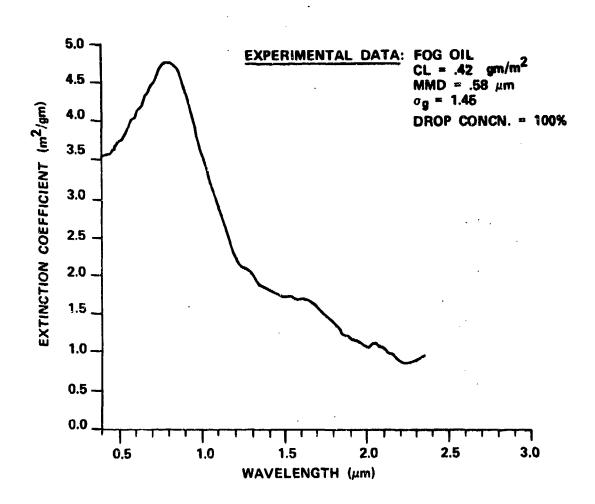


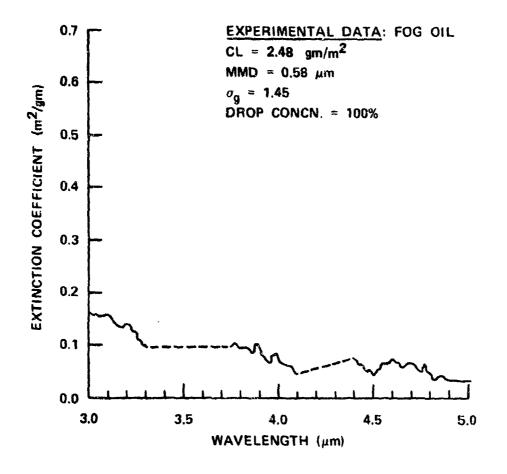
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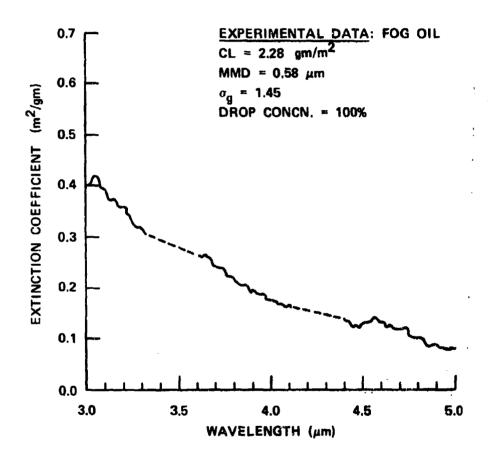


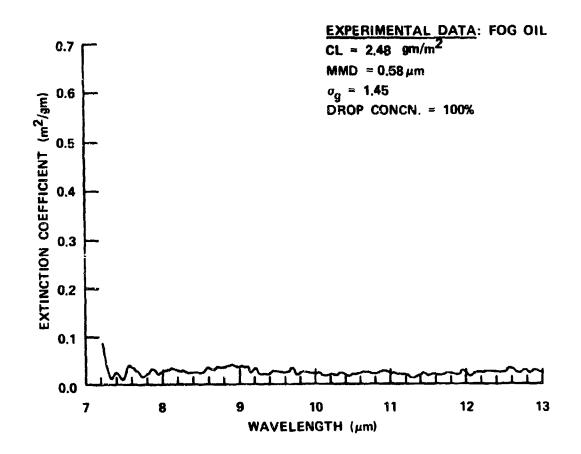
# VII. FOG OIL SMOKE (LOW-VOLATILITY HYDROCARBON DISTILI.ATE) EXPERIMENTAL DATA.

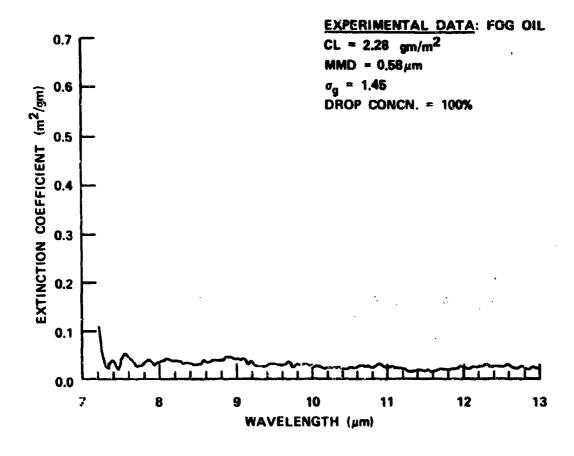
1. Fog Oil Smoke, 0.4 to 2.4 μm, 3 to 5 μm, and 8 to 13 μm (IMBIBER BEAD DEVICE), Test Date: 2 December 1975.

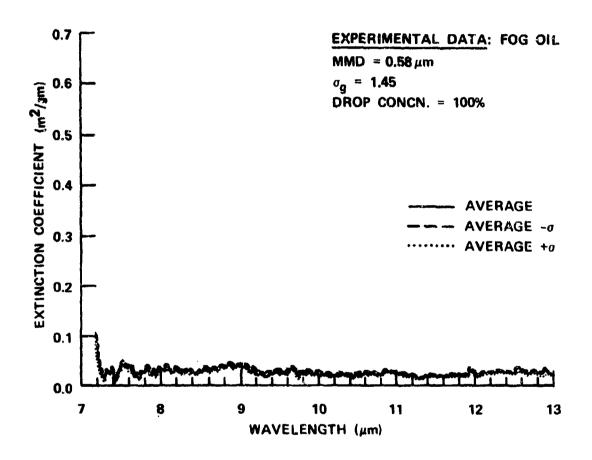




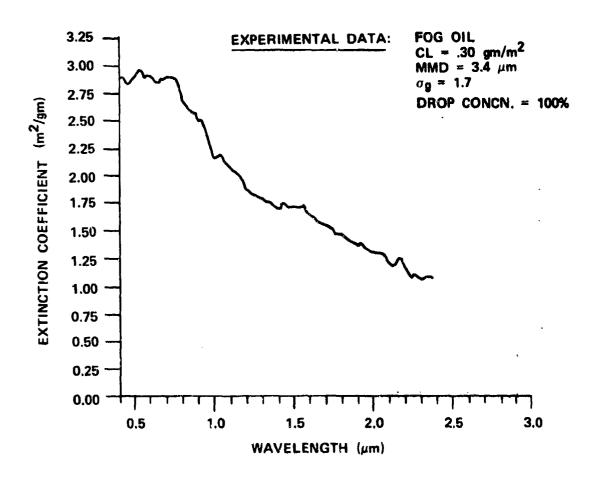


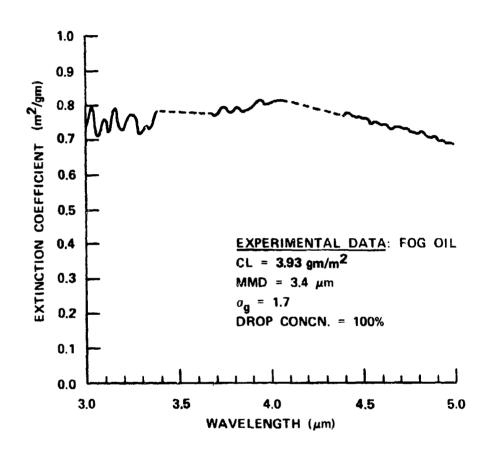


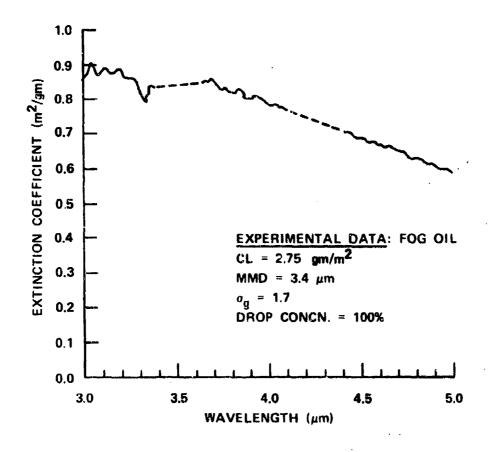


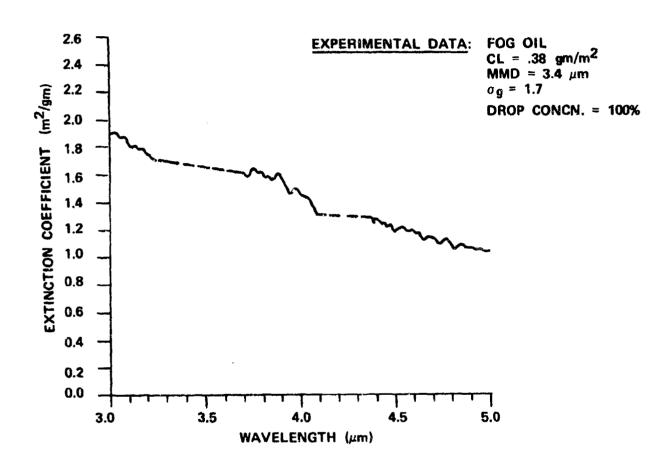


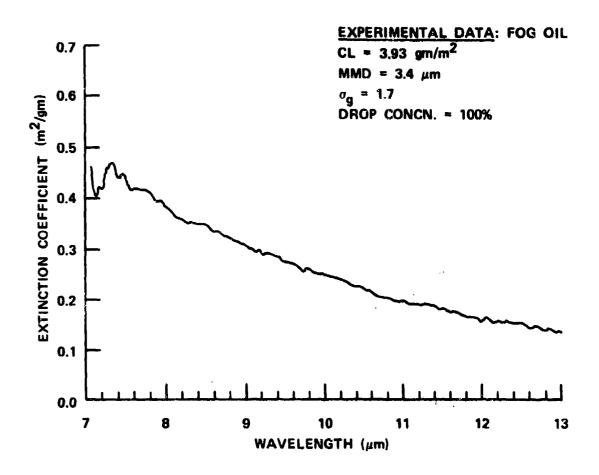
2. Fog Oil Smoke, 0.4 to 2.4  $\mu$ m, 3 to 5  $\mu$ m, and 8 to 13  $\mu$ m (HOT PLATE DISSEMINATION), Test Date: 5 December 1 75.

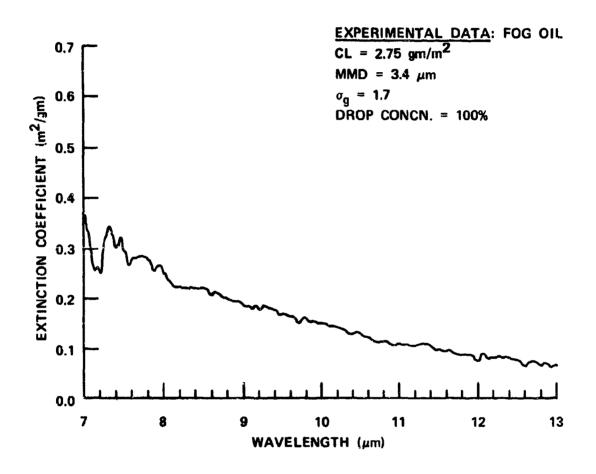


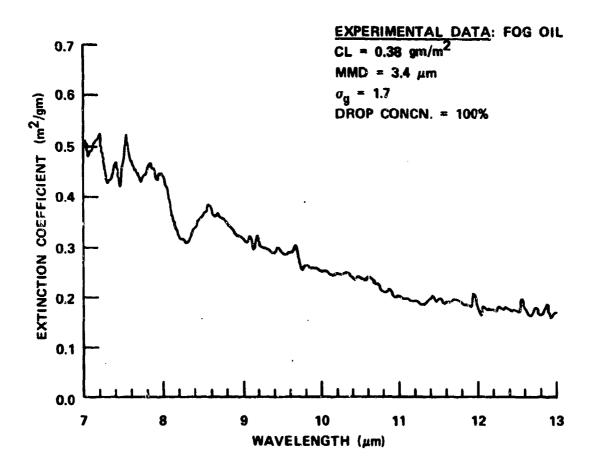


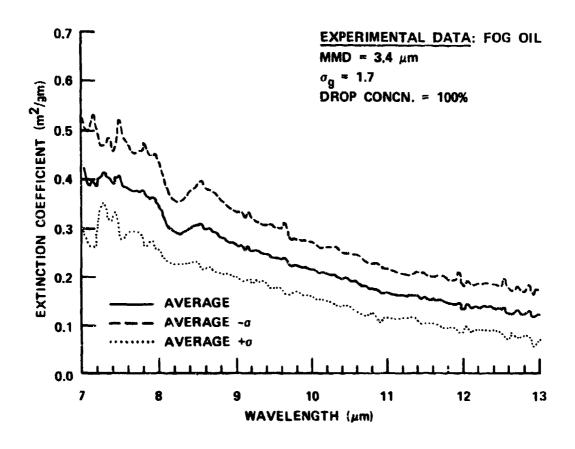












## APPENDIX A

### SMOKE MATERIALS AND DISSEMINATION METHODS

Smoke designator	Smoke agent	Dissemination methods	Droplet composition
RP	Red phosphorus	Burning	H <sub>3</sub> PO <sub>4</sub> solution
FS	Chlorosulfonic acid + free SO <sub>3</sub>	Spraying	H <sub>2</sub> SO <sub>4</sub> solution
НС	Zinc oxide, aluminum hexachloroethane	Pyrotechnic	ZnCl <sub>2</sub> solution
Fog oil	Low volatility hydrocarbon distillate	Pyrotechnic	Low volatility hydrocarbon distillate
Fog oil	Low volatility hydrocarbon distillate	Dripping on hot surface (Test of 5 Dec 75 only)	Low volatility hydrocarbon distillate

#### APPENDIX B

### RADIATION TRANSPORT MODELING

The theory developed in the following paragraphs summarizes the Mie modeling of radiation transport through an aerosol cloud of monodisperse particles and indicates the relationship of experimentally determined quantities to the model. The theory for monodisperse aerosols is developed, as a special case, from the general polydisperse theory.

The transmittance, T, through a cloud of aerosol particles is given by

$$T = e^{-\gamma L}$$
 (B-1)

where

 $\gamma$  = total extinction coefficient per unit length

L = path length

and

$$\gamma = \int_{0}^{\infty} G_{e}(D)N(D)dD$$
 (B-2)

where there are N(D)dD particles per unit volume in the interval dD so that

$$N_{O} = \int_{O}^{\infty} N(D)dD$$
 (B-3)

is the total number of particles per unit volume and  $G_e(D)$  is the extinction cross section. In terms of the efficiency factor  $Q_e(D)$ 

$$G_e(D) = \frac{\pi D^2}{4} Q_e(D)$$
 (B-4)

so that

$$\gamma = \int_{0}^{\infty} \frac{\pi D^2}{4} Q_e(D) N(D) dD$$
 (B-5)

If the aerosol is monodisperse

$$\gamma = \frac{\pi D^2}{4} Q_e N_c = \frac{\pi D^2}{4} Q_e \frac{N}{V}$$
 (B-6)

and

$$T = e^{-\pi D^2 Q} e^{NL/4V}$$
 (B-7)

Consider taking a sample from the test chamber of N monodisperse aerosol particles with diameter. D, which are contained in the sampling volume, V. The mass concentration is given by:

$$C = M_f/V (B-8)$$

where  $M_f$  = mass of aerosol material collected on the filter. In terms of N, D,  $\rho$  (the density of the sampled material), and  $V_p = \frac{\pi D^3}{6}$  the volume of a single particle,  $M_f$  is given by

$$M_{f} = \frac{\pi}{6} D^{3} \rho N \tag{B-9}$$

Therefore, the mass concentration is given by

$$C = \frac{\pi D^3 \rho N}{6V}$$
 (B-10)

Solving (B-10) for N/V and substituting into B-7 we get

$$T = e^{\frac{-3Q_eCL}{2\rho D}}$$
 (B-11)

Recalling that  $T = I/I_0$  where I and  $I_0$  are, respectively, the transmitted intensities with and without aerosol present we get

$$I/I_{C} = e^{-aCL}$$
 (B-12)

where  $\alpha = \frac{3Q_e}{2\rho D}$  and is known as the extinction coefficient. These last two relationships provide the interface between the model and experiment since  $Q_e$  can be calculated from Mie theory and I,  $I_o$ , C,  $\rho$ . D. and L can be measured.